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## **TAILOR MAKING HIGH PERFORMANCE GRAPHITE FIBER REINFORCED PMR POLYIMIDES**

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# TAILOR MAKING HIGH PERFORMANCE

## GRAPHITE FIBER REINFORCED PMR POLYIMIDES

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### ABSTRACT

Studies performed to demonstrate the feasibility of using the polymerization of monomer reactants (PMR) approach to "tailor make" processable polyimide matrix resins are described. Monomeric reactant solutions containing the dimethyl ester of 3,3',4,4'-benzophenonetetracarboxylic acid, 4,4'-methylenedianiline and the monomethyl ester of 5-norbornene-2,3-dicarboxylic acid were used to impregnate Hercules HTS graphite fiber. Six different monomeric reactant stoichiometries were studied. The processing characteristics and elevated temperature mechanical properties of the PMR polyimide/HTS graphite fiber composites are described.

### INTRODUCTION

The resins currently being used as matrices in the vast majority of advanced fiber composites are epoxy resins. Fiber reinforced epoxy resins can easily be processed into a variety of hardware items. However, the upper use temperature of epoxies is limited to a maximum of 350<sup>0</sup> F. In addition, the elevated temperature mechanical properties of graphite fiber/epoxy composites are degraded during long-term exposure of the composites to humid environments. Therefore, a matrix resin needs to be developed which has the processability of epoxies, higher use temperatures than epoxies and greater moisture resistance than epoxies.

Prior studies conducted in our laboratories (refs. 1 to 3) and elsewhere (ref. 4) have demonstrated the effectiveness of PMR (in situ polymerization of monomer reactants on the surface of reinforcing fibers)

methodology for preparing high temperature resistant fiber reinforced polymer matrix composites. These earlier studies (refs. 1 to 4) were concerned with the development of composites for continuous use in air at 600<sup>0</sup> F. Therefore, monomer compositions and stoichiometries were selected which would lead to addition-type polyimides having the best over-all balance of processability and thermo-oxidative stability. The trade-off between processing characteristics and thermo-oxidative stability necessitated using monomer compositions and stoichiometries which provided lower flow characteristics than normally obtained from epoxy resins. The studies reported in reference 2 showed that PMR methodology is a facile method for introducing molecular structural variations into the polymer matrix. The monomer compositions and stoichiometries previously studied provided a fairly broad range of properties together with moderate variations in flow characteristics. Therefore, it is hypothesized that the PMR approach can be used to select monomer compositions and or stoichiometries which provide higher flow polyimides for use at temperatures well above the upper use temperature of epoxy resins.

This report describes a study to establish the validity of the aforesaid hypothesis. If the hypothesis is proven to be correct, then it should be possible to use the PMR approach for the "tailor making" of polyimide matrices.

Composites were fabricated from Hercules HTS graphite fiber and PI based on the monomers 5-norborene-2,3-dicarboxylic acid monomethyl ester (NE), dimethyl ester of 3,3',4,4'-benzophenonetetracarboxylic acid (BTDE) and 4,4'-methylenedianiline (MDA). Formulated molecular weights (FMW) in the range of 1000 to 1500 were investigated. Resin flow characteristics and composite properties were determined. Composite mechanical properties were determined at room temperature, 450<sup>0</sup> and 550<sup>0</sup> F. Composite weight loss and mechanical properties retention characteristics as a function of exposure time and elevated temperature were also determined.

## EXPERIMENTAL PROCEDURE

### Monomeric Reactant Solutions

The monomers used in this study are shown in table I. The monomethyl ester of 5-norbornene -2,3-dicarboxylic acid (NE) and 4,4'-methylenedianiline (MDA) were obtained from commercial sources. The dimethyl ester of 3,3',4,4'-benzophenonetetracarboxylic acid (BTDE) was synthesized by refluxing a suspension of 3,3',4,4'-benzophenonetetracarboxylic dianhydride (96.6 g,  $3.00 \times 10^{-1}$  mole) in anhydrous methanol (170 ml) until the solid had dissolved (2 to 3 hr) and then for an additional hour, resulting in a 50 weight percent BTDE/methanol solution. Reactant solutions were prepared at a solids loading of 50 weight percent in methanol. The stoichiometry of the reactants was governed by the desired formulated molecular weight.

### Composite Fabrication

Prepreg tapes were made by drum winding and impregnating Hercules HTS graphite fiber with the various solutions of monomeric reactants to yield prepregs that contained 45.5 percent monomers and 54.5 percent fiber by weight. The prepreg made from monomer solutions were air dried on the drum at room temperature for 1 hour and then 2 hours at 120° F to reduce the solvent content to approximately 10 percent by weight. After this treatment, the prepregs remained flexible, but not tacky. The prepreg tapes were then removed from the drum, cut into 3 by 10 inch plies and stacked unidirectionally, 9 plies thick, into a preforming mold. The stacked prepreg was staged at 400° F for 2 hours under an applied pressure of 0.3 psi. Composites were then molded by placing the staged prepreg into a matched metal die preheated to 500° F. Following a dwell time, which ranged from 45 to 90 seconds, 1000 psi was applied for 60 minutes. After curing, the composites were post-cured by placing them directly into a 600° F oven for 16 hours. Resin flow was determined by weight difference prior to final cure and after the cure with resin flash removed.

## Composite Testing

Prior to specimen preparation all laminates were inspected using the ultrasonic C scan technique (ref. 5). Flexural strength tests were performed using a 3 point loading fixture with a fixed span of 2 inches. The thicknesses of the laminates ranged from 0.070 inch to 0.090 inch. The resultant span/depth ratio used ranged from 22 to 28. The rate of center loading for flexural testing was 0.05 inch/min. Interlaminar shear strength tests were conducted at a constant span/depth ratio of 5. Elevated temperature tests were performed in an environmental heating chamber. For the flexural and shear tests the load was applied after a 15 minute soak at the test temperature. Forced convection air ovens were used for the long-term isothermal exposure at 450<sup>0</sup> and 550<sup>0</sup> F. Composite weight measurements were made throughout the exposure time period. The air change rate was 100 cubic centimeters per minute.

The properties data presented are averages of 3 or more tests at each condition. Fiber content was determined for all laminates and ranged from 53 to 65 volume percent. For flexural tests all results were normalized to 55 volume percent fiber.

## RESULTS AND DISCUSSION

The monomeric reactant stoichiometries used in this study are given in table II. The number of moles of the monomeric reactants in each of the monomeric solutions was governed by the following ratio:

$$n : (n + 1) : 2$$

Where  $n$ ,  $(n + 1)$  and 2 are the number of moles of BTDE, MDA and NE, respectively. The formulated molecular weight (FMW) given in the table is considered to be the average molecular weight of the imidized prepolymer that could have been formed if amide-acid prepolymer had been synthesized. The equation for FMW is:

$$\begin{aligned} \text{FMW} = n \text{ MW}_{\text{BTDE}} + (n+1) \text{ MW}_{\text{MDA}} \\ + 2 \text{ MW}_{\text{NE}} - 2(n+1) \text{ MW}_{\text{H}_2\text{O}} + \text{MW}_{\text{CH}_3\text{OH}} \end{aligned} \quad (1)$$

where  $\text{MW}_{\text{BTDE}}$ ,  $\text{MW}_{\text{MDA}}$  etc. are the molecular weights of the indicated reactants and by-products. It is now common practice to denote the stoichiometry of a PMR resin made from BTDE, MDA and NE as PMR FMW/100. For example, PMR 15 denotes the polyimide prepared from BTDE, MDA and NE with the stoichiometry adjusted so that the FMW = 1500.

The effect of FMW on percent resin flow is shown in figure 1. It can be seen that the resin flow increased significantly (from 3 to 20 percent) as the FMW was decreased from 1500 to 1000. These results clearly show that the resin flow characteristics of PMR polyimides can be varied over a wide range or "tailor made" to meet specific requirements. It is important to note that ultrasonic C scan examination of the laminates revealed them to be void free. The resin flow results show the sensitivity of resin flow to imide ring content. As the number of imide rings was decreased by 33 percent (from 6 rings to 4) in going from PMR 15 to PMR 10, the resin flow increased by nearly 600 percent.

Figure 2 shows the variation of percent resin weight loss as a function of matrix FMW for PMR/HTS graphite fiber composites after exposure in air for 600 hours at 450° and 550° F. The results show that all of the PMR composites exhibited excellent thermo-oxidative stability (TOS) at 450° F. The resin weight loss at 450° F for the higher resin flow PMR compositions (PMR 10 to PMR 13) was less than 2 percent. At 550° F the resin weight loss of PMR compositions in the FMW range of 1000 to 1400 was appreciably higher than for PMR 15. Earlier studies (ref. 2) identified PMR 15 as the PMR polyimide matrix resin possessing the best over-all balance of processing characteristics and 600° F TOS. The superior TOS of PMR 15 at temperatures in the range of 550° to 600° F can be attributed to the low alicyclic content of PMR 15 as shown in table II. The percentage of alicyclic material is given by the following equation:

$$\text{Percent alicyclic} = \frac{2[MW_{NE} - (MW_{COOH} + MW_{COOCH_3})] \times 100}{FMW} \quad (2)$$

Where  $MW_{COOH}$  and  $MW_{COOCH_3}$  are the molecular weights of carboxyl and methyl ester groups, respectively.

The resin flow and weight retention data presented in figures 1 and 2 support the hypothesis that the PMR approach can be used to select monomer stoichiometries which provide high flow PMR polyimides for use at temperatures above the use temperature for epoxy resins. Isothermal gravimetric analysis data are not sufficient to permit specification of a material's upper use temperature. It is more important to consider the material's retention of mechanical properties after extended exposure at elevated temperatures and to compare these data to design requirements.

The variation of composite flexural strength for the various PMR compositions reinforced with Hercules HTS graphite fiber as a function of FMW is shown in figure 3. Results are shown for specimens tested at room temperature and at 450° and 550° F after short-term (15 min) exposure in air at the indicated test temperature.

The room temperature flexural strength ranged from 223 000 psi at an FMW of 1000 to 200 000 psi at an FMW of 1500. It is important to note that at 450° and 550° F the composites exhibited excellent retention of room temperature flexural strength throughout the FMW range investigated. The retention levels at 450° F ranged from 75 to 88 percent and at 550° F from 70 to 78 percent. In contrast the highest retention level at 350° F for graphite fiber/epoxy composites is generally considered to be 55 percent.

It can be seen in figure 3 that the room temperature, 450° and 550° F properties decreased as FMW was increased. The influence of matrix modulus and ultimate strength on composite flexural strength was discussed in reference 6. Because the cure of PMR polyimides involves a complex addition reaction of the alicyclic chain-ends resulting in chain extension and cross-linking, resin matrices having decreased cross-link densities, and therefore, decreased moduli result from increases in FMW. The room temperature results reflect the effect of

matrix modulus. The 450° and 550° F results reflect the combined effects of matrix modulus and temperature.

Figure 4 shows the variation of room temperature, 450° and 550° F (short-time) interlaminar shear strength (ILSS) with FMW. It was pointed out in reference 6 that composite ILSS is strongly influenced by the modulus, proportional limit strain and ultimate strength of the matrix. Therefore, it can be speculated that the variation of ILSS with FMW at any given temperature reflects the net effect of the various matrix properties. The more important point to be made is that the composites retained a high level of ILSS at 450° and 550° F throughout the range of FMW investigated. The ranges for the retention levels at 450° and 550° F were 66 to 75 percent and 57 to 61 percent, respectively.

Figures 5 and 6 show the variation of flexural strength and ILSS, respectively, with exposure time (maximum of 600 hours) for PMR 10 graphite fiber composites exposed and tested at 450° and 550° F. Data showing the effects of isothermal exposure on flexural strength and ILSS were also collected for the PMR graphite fiber composites made from the other FMW compositions. It can be seen in figures 5 and 6 that the PMR 10 composites exhibited excellent retention of mechanical properties throughout the 600 hour exposure time. Similar retention characteristics were displayed by the other graphite fiber reinforced PMR compositions.

In figure 7 the short-time (15 min) elevated temperature properties are compared with the long-time (600 hr) elevated temperature properties over the range of FMW. The data from the tests conducted at 450° F are shown in figures 7a and 7b for flexural strength and ILSS, respectively. Figures 7c and 7d show the results from the tests conducted at 550° F.

The comparisons presented in figure 7 clearly illustrate the superior elevated temperature properties retention characteristics of the PMR polyimide matrix resins at temperatures up to 550° F. With the exception of the data from the FMW compositions of 1000 and 1100 the short-time and long-time data for a given property and temperature are quite comparable. By comparing figure 7a with figure 7b it can also be seen that the 450° and 550° F properties do not differ appreciably.



The mechanical property data, together with the resin flow and weight retention characteristics have, in our opinion, established the validity of the hypothesis that the PMR approach can be used to "tailor make" high flow polyimides with higher use temperatures than epoxy resins.

### CONCLUDING REMARKS

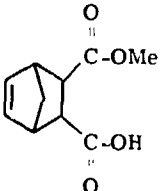
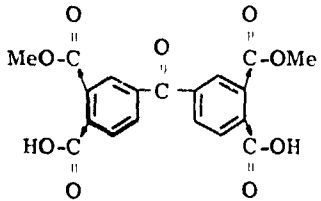
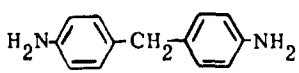
The in situ polymerization of monomer reactants (PMR) approach can be used to "tailor make" fiber reinforced addition-type polyimides having specified resin flow characteristics and excellent retention of mechanical properties after long-term exposure in air in the 450° to 550° F temperature range. By adjusting the monomeric reactant stoichiometry the resin flow characteristics can be varied over a wide range and in this way a product can be achieved which meets specific requirements. The PMR compositions investigated in this study provided flow values in the range of 3 to 20 percent. After 600 hours of exposure at 450° or 550° F the composite properties determined at the exposure temperature were comparable to the short-time elevated temperature properties. The short-time elevated temperature properties, in turn, compared favorably with room temperature properties.

The excellent processability and thermo-oxidative stability of high flow PMR polyimides suggests that these materials have excellent potential as matrix resins both within and above the use temperature range of epoxy resins.

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TABLE I. - MONOMERS USED FOR POLYIMIDE SYNTHESIS

Structure	Name	Abbreviation
	Monomethyl ester of 5-norbornene-2,3-dicarboxylic acid	NE
	Dimethyl ester of 3,3',4,4'-benzophenone-tetracarboxylic acid	BTDE
	4,4'-Methylenedianiline	MDA

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TABLE II. - MONOMER STOICHIOMETRY

Formulated molecular weight	Moles of BTDE, <sup>a</sup> (n)	Percent alicyclic content
1000	1.054	9.20
1100	1.260	8.37
1200	1.465	7.67
1300	1.672	7.08
1400	1.880	6.57
1500	2.087	6.13

<sup>a</sup>Molar ratio of BTDE/MDA/NE equals

$$n : (n + 1) : 2$$

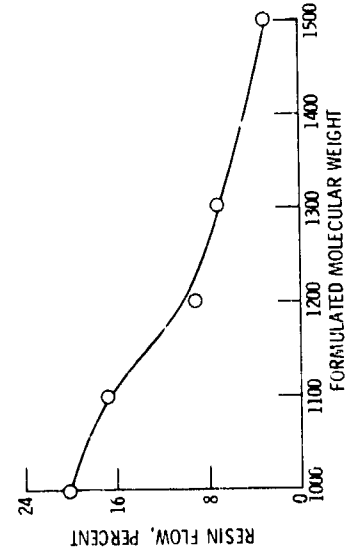


Figure 1. - Percent resin flow as a function of matrix formulated molecular weight for PMR PI/HTS graphite fiber composites.

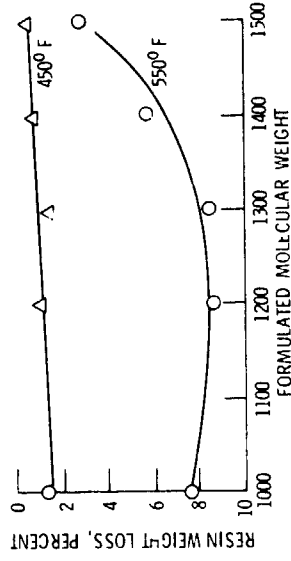


Figure 2. - Percent resin weight loss as a function of matrix formulated molecular weight for PMR PI/HTS graphite fiber composite after exposure in air for 600 hr at 450° and 550° F.

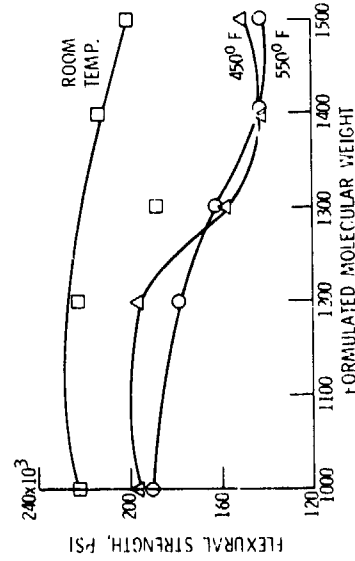


Figure 3. - Flexural strength of PMR PI/HTS graphite fiber composites as a function of matrix formulated molecular weight. Tests conducted at room temperature and at 450° and 550° F after short-time (15 min) exposure at indicated test temperature.

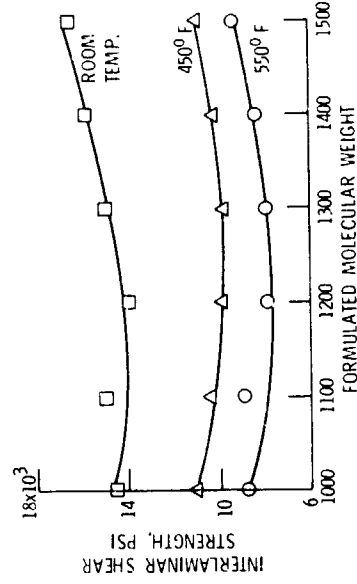


Figure 4. - Interlaminar shear strength of PMR PI/HTS graphite fiber composites as a function of matrix formulated molecular weight. Tests conducted at room temperature and at 450° and 550° F after short-time exposure at indicated test temperature.

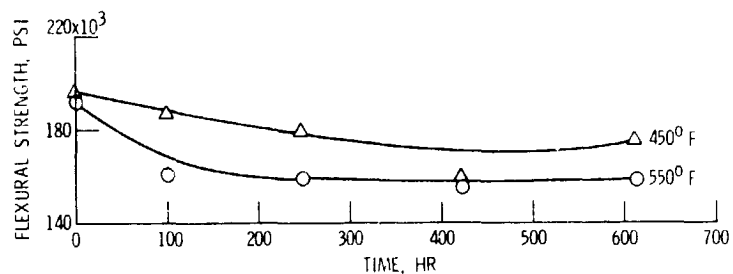


Figure 5. - Flexural strength of FMW 1000 PMR PI/HTS graphite fiber composites exposed and tested at 450° and 550° F.

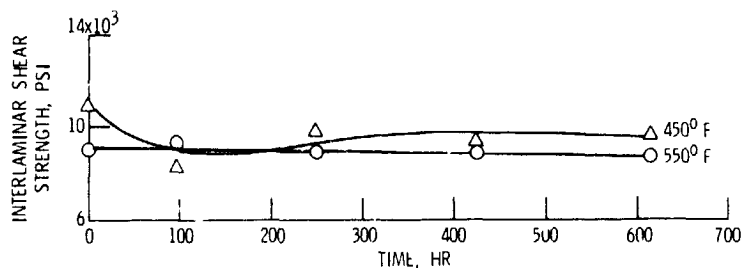
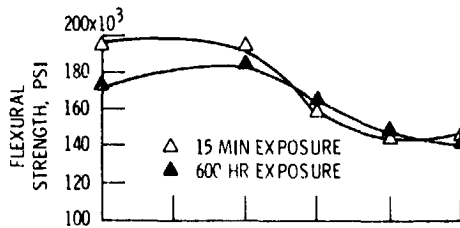
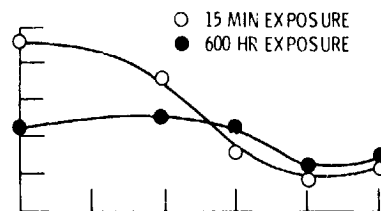


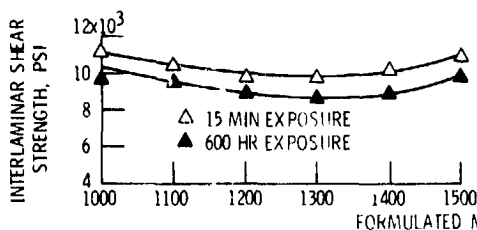
Figure 6 - Interlaminar shear strength of FMW 1000 PMR PI/HTS graphite fiber composites exposed and tested at 450° and 550° F.



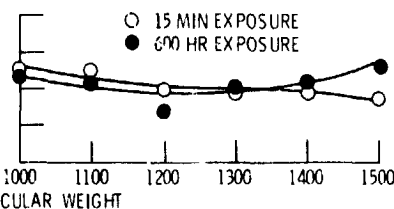
(a) 450° F FLEXURAL STRENGTH.



(b) 550° F FLEXURAL STRENGTH.



(c) 450° INTERLAMINAR SHEAR STRENGTH.



(d) 550° F INTERLAMINAR SHEAR STRENGTH.

Figure 7. - Long-time and short time elevated temperature properties of PMR PI/HTS graphite fiber composites.